

Frontiers in actinide metal physics: the role of partially localized 5f electrons

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It has long been recognized that the anomalous behaviour of the 5f electrons in plutonium is central to its complex metallurgy and interesting physical properties (for a recent review, see [1]). In recent years, a significant renaissance has occurred in actinide metal physics, improving our understanding, but in some cases also deepening the mysteries of plutonium. While various theoretical models characterize the phenomena differently, a common theme in modern electronic structure calculations is some form of partial localization of the 5f electrons in plutonium. One simple approach is to consider plutonium as magnetically ordered. While no experimental evidence exists to support a magnetically ordered ground state for Pu [2], spin fluctuations may be important. Apparent proximity to magnetic order is also a common theme in strongly correlated electron systems such as the heavy fermion materials. A particular manifestation of this is the relatively high-transition-temperature superconductivity observed in PuCoGa₅ [3] and its apparent similarity to the cuprate superconductors [4].

In this talk, we review what is known about the normal state properties of metallic plutonium and its intermetallic compounds, including recent insights due to advances in experimental techniques and to the discovery of novel materials. The frontiers of actinide metal physics hold much potential for further breakthroughs that will impact our broader understanding of electron correlation phenomena.

Work at Los Alamos performed under the auspices of the U.S. Department of Energy.

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Plutonium Encaged: Pu(IV) and Model Ce(IV) Maltol Complexes

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The coordination chemistry of plutonium remains relatively unexplored. Thus, the fundamental coordination chemistry of plutonium is being studied using simple multi-dentate ligands with the intention that the information gleaned from these studies may be used in the future to develop plutonium-specific sequestering agents. Towards this goal, hard Lewis-base donors are used as model ligands. Maltol, an inexpensive natural product used in the commercial food industry, is an ideal ligand because it is an all-oxygen bidentate donor, has a rigid structure, and is of small enough size to impose little steric strain, allowing the coordination preferences of plutonium to be the deciding geometric factor. Additionally, maltol is the synthetic precursor of 3,4-HOPO, a siderophore-inspired bidentate moiety tested by us previously as a possible sequestering agent for plutonium under acidic conditions. As comparisons to the plutonium structure, Ce(IV) complexes of the same and related ligands were examined as well. Cerium(IV) complexes serve as good models for plutonium(IV) structures because Ce(IV) has the same ionic radius as Pu(IV) (0.94 Å).^{1,2}

Plutonium(IV) maltol crystals were grown out of a methanol/water solution by slow evaporation to afford red crystals that were evaluated at the Advanced Light Source at Lawrence Berkeley National Laboratory using single crystal X-ray diffraction. Cerium(IV) complexes with maltol and bromomaltol³ were crystallized via slow evaporation of the mother liquor to afford tetragonal, black crystals. All three complexes crystallize in space group $I4_1/a$. The Ce(IV) complex is isostructural with the Pu(IV) complex, in which donating oxygens adopt a trigonal dodecahedral geometry around the metal with the maltol rings parallel to the crystallographic S_4 axis and lying in a non-crystallographic mirror plane of D_{2d} molecular symmetry (Fig 1). The metal-oxygen bonds in both maltol complexes are equal to within 0.04 Å for each oxygen type. In contrast to the maltol structures, the cerium(IV)

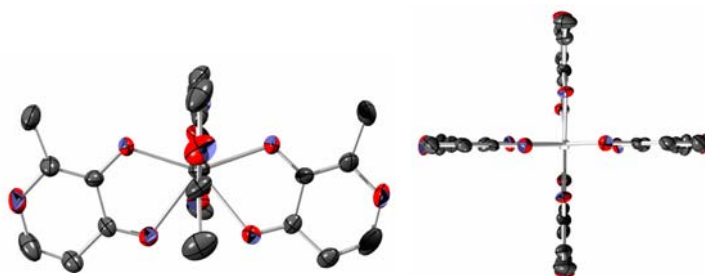


Fig 1: Crystal structures of Pu(IV)(maltol)₄ viewed from the side (left) and down the S_4 axis (right).

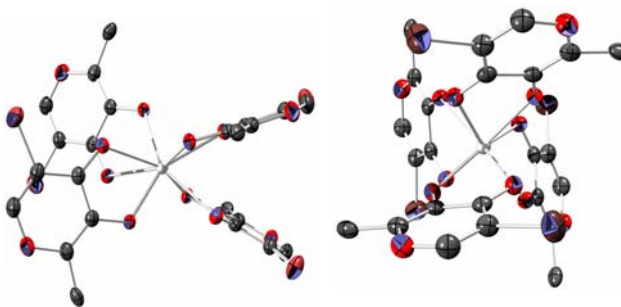


Fig 2: Crystal structures of Ce(IV)(bromomaltol)₄ views from the side (left) and down the S_4 axis (right).

bromomaltol complex arranges the maltol rings in a drastically different manner while maintaining the S_4 crystallographic symmetry (Fig 2). The coordination geometry around the cerium remains a trigonal dodecahedron, but the chelating ligands span a different set of edges as in the maltol structures; the two-fold related bromomaltol ligands twist away from planarity, breaking the D_{2d} molecular symmetry. It is unlikely that steric interaction with a bromine on the same molecule would have caused the observed rearrangement, as there would be sufficient separation between them to accommodate their bulk in the geometry of the plutonium and cerium maltol complexes. The extended packing in the unit cell of both the plutonium and cerium maltol crystals indicates that pi stacking occurs throughout the lattice via the maltol rings with close contacts between rings of approximately 3.6 Å. Introduction of the bromine to this structure would disrupt the packing that would allow these interactions, causing the molecule to adopt the geometry present in the bromomaltol structure. In this unexpected arrangement the complex is still able to maintain some pi stacking with the maltol rings of adjacent molecules with a close contact of approximately 3.3 Å. Additionally, the bromine on each ligand is arranged such that its next closest contact is with a bromine 3.64 Å away on another molecule. Despite the different ligand geometry, the bromomaltol structure exhibits metal-oxygen bond distances that are within 0.06 Å of those in the maltol complexes.

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Plutonium Metallurgy: The materials science challenges bridging condensed-matter physics and chemistry

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The origins of physical metallurgy have been traced back to the highlands of western Asia northwest of the Persian Gulf as early as the year 4300 BC.¹ By 2000 BC, smelting, melting, casting, annealing, and forming of metals such as gold, silver, copper, lead, and iron had been practiced. Between 2000 BC and 1800 AD, advances in metallurgy impacted society in the areas of the arts, agriculture, industry, and military applications. By the nineteenth century, the industrial need for steel drove metallurgy to become an important discipline connecting chemistry, physics, and mechanics. Matthiessen's rule, based on an 1867 electrical conductivity investigation, is credited as the beginning of "physics of metals", solid-state physics, and now condensed-matter physics. Phase diagram investigations, the development of the constitution of alloys, and the principles of heterogeneous equilibria by Willard Gibbs were first published in 1876. Around the same time, physical chemistry was laying the basis for the study of phase transformation kinetics. Thus, by the end of the 19th century, metallurgy had established its role in the interspace between condensed-matter physics, chemistry, and crystallography.

In the 20th century, tremendous advances in metallurgy were made possible by von Laue's 1912 discovery of diffraction of x-rays and the subsequent developments by Bragg and others. This technology opened the door to crystallographic and microstructural studies of metals and alloys and the discovery of superlattice structures, Hume-Rothery alloys, Laves compounds, and the importance of point defects. Furthermore, significant developments in the understanding of solidification, nucleation and growth theory, plasticity, texture, failure, martensitic phase transformations, diffusion, and many other physical and mechanical properties of metals and alloys were made. Scientific advances in metallurgy clarified the understanding that processing of metals was responsible for setting the microstructure, and the microstructure was closely related to the performance of metals. Thus, microstructure-properties-processing relationships became the central component of 21st century metallurgy.

The understanding of metallurgy gained over the previous four millennia was vital for learning how to process and characterize the new element plutonium when it was fabricated by Seaborg, Kennedy, and Wahl in 1942.² The earliest stages in Pu metallurgy were motivated by the need to produce a product; at that time, quantity took precedence over quality. Problems with consistent density and phase transformations led C.S. Smith to suggest intentionally alloying Pu and ultimately, an alloy of 3.0 to 3.5 atomic percent Ga was used in the Trinity test.³ From 1945 onward, a tremendous amount of effort was placed on phase diagrams and phase stability. Bochvar *et al.*,⁴ Ellinger *et al.*,⁵ Zachariasen and Ellinger,⁶ Chebotarev *et al.*,⁷ Ward *et al.*,⁸ Hecker and Timofeeva,⁹ and many others contributed significantly to the understanding of crystal structures, phase diagrams, and phase stability. In the last two decades, the motivation for Pu science has shifted. No longer is the sole purpose to produce a product. Today, Pu science is more focused on understanding the fundamental relationships between electronic structure, crystallographic phase stability, and the roles of microstructure, impurities, and defects. In the

last few years, the need to understand the aging of Pu has dictated much of the science. The continuous radioactive decay of Pu produces an array of impurity daughter products that accumulate with age. How the damage introduced by radioactive decay and the resulting impurities affect metallurgical aspects of Pu, such as phase transformations and magnetic properties are areas of intense research.

Today, the boundaries between metallurgy, condensed matter physics, and physical chemistry in the study of Pu are blurred. Recent advances in our understanding of this intriguing material are being made in all areas of physical science. This presentation will highlight these exciting advances and focus on the significant challenges in the field of Pu metallurgy. Among the topics to be discussed are phase transformations and phase stability. Although there have been significant advances in our understanding of the phase diagram, even after 40+ years, the nature of the double-C curve in the time-temperature-transformation (TTT) diagram remains unresolved. Advances have been made in our knowledge of the $\delta \rightarrow \alpha'$ transformation,¹⁰⁻¹³ but less is known about the mechanism and kinetics of the α to β and reverse transformation during temperature or pressure excursions. Natural aging of Pu has been the focus of significant recent efforts,¹⁴ but we still do not fully know the mechanism(s) of delta phase stability,¹⁵ the vacancy migration energy, and the mechanism that appears to limit the size of the helium bubbles that form from the alpha decay of Pu into U and He.

With thousands of years of accumulated metallurgical knowledge of most every element in the periodic table, we substantially understand most metals. However, the 21st century finds us still perplexed by the deeply complex structure-properties-processing relations in Pu. This is a very exciting time to be engaged in Pu metallurgy. With ever-improving computational capabilities and significant focus on electronic structure calculations and experiments, there are now collaborative worldwide contributions to our understanding.

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Scientific Understanding Aids Plutonium Remediation at Rocky Flats.

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BACKGROUND

The Rocky Flats Environmental Technology Site (RFETS) was a U.S. Department of Energy (DOE) environmental cleanup site located about 15 miles northwest of downtown Denver. More than 2.5 million people live within a 50-mile radius of the site, and 300,000 of those live in the Rocky Flats watershed. From 1952 - 1989, the Rocky Flats Plant made components for nuclear weapons using various radioactive and hazardous materials, including plutonium and uranium; toxic metals such as beryllium; and hazardous chemicals, such as cleaning solvents and degreasers. In 1989, Rocky Flats was raided by the FBI/EPA for alleged environmental violations, and all nuclear operations were suspended. Nearly 40 years of nuclear weapons production left behind a legacy of contaminated facilities, soils, surface and ground water. RFETS was designated as an EPA Superfund cleanup site, and in March of 1995, DOE's Baseline Environmental Management Report called for the site to be closed by the year 2060 at a cost in excess of \$37 billion.

In May of 1995, wet spring conditions and intense rainfall events at the site caused Site personnel and stakeholder groups to raise concerns about the potential for increased plutonium mobility in the RFETS environment, and the potential for increased plutonium transport offsite onto public lands. These events placed increased emphasis on the potential for soluble forms of plutonium in surface and ground waters in order to account for the appearance of plutonium at monitoring stations at the Site boundary. The accepted DOE model for risk assessment (RESRAD) assumed transport of soluble forms of contaminants, and required input of distribution coefficients (K_d) between aqueous and soluble phases. When plutonium K_d 's were input into the model, it predicted no plutonium transport, in disagreement with the observed plutonium behavior. This situation led to public mistrust and lack of confidence. When coupled with other questions regarding the mobility of different actinide elements (U, Pu, Am) at different Site locations, this situation prompted DOE and Kaiser-Hill to establish the Actinide Migration Evaluation (AME) advisory group in 1996. The group was formed to provide guidance on issues of actinide behavior and mobility in the air, surface water, groundwater, and soil.

Through a combination of expert judgement and state-of-the-art scientific measurements, it was shown that under environmental conditions at Rocky Flats, plutonium and americium form insoluble oxides. These insoluble materials are attached to natural soil organic and mineral particles that can migrate in the Rocky Flats environment by wind and surface water sedimentation/resuspension processes. This scientific understanding demonstrated that soluble transport models were not appropriate, and led to the development and application of large-scale erosion/sediment transport models. The scientific understanding developed through these integrated studies

contributed directly to the basis for plutonium and americium cleanup levels in soils and concretes. It helped all parties focus remediation efforts on surficial contamination and transport pathways (wind and surface water erosion) that posed the greatest risk to human health and the environment. It helped guide selection of surface-specific removal technologies and future land configuration strategies. Thus scientific understanding through advanced measurement techniques was developed into science-based communication and decision-making for Kaiser-Hill and DOE that helped focus Site-directed efforts in the correct areas, and aided the DOE in its effort to close the RFETS. On October 13, 2005, Kaiser-Hill Company declared to DOE the physical completion of the Rocky Flats Closure Project, culminating a 10-year, \$7 billion project – ultimately delivering nearly \$30 billion in taxpayer savings.

An overview of the Rocky Flats Site, the technical issues, the scientific experiments, the transport models, the environmental cleanup, and the final land configuration will be presented.

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PuCoGa₅ and Related Materials

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Superconductivity in actinide-bearing compounds has served as a tool for guiding an interpretation of the role that 5f-electrons play in determining physical properties. Likewise, an interpretation of the mechanism of superconductivity must be consistent with what is known about the normal-state properties of these compounds. PuCoGa₅, the first Pu-based superconductor¹, exemplifies these complementary approaches to revealing the nature of plutonium's 5f-electrons in this compound. Its superconducting transition temperature T_c of 18.5K is nearly an order of magnitude higher than that of any previously known 5f-electron material but comparable to T_c 's found in some transition-metal intermetallic compounds. Unlike these other intermetallics whose superconductivity is conventional, i.e., mediated by an attractive electron-phonon interaction, the uniform magnetic susceptibility of PuCoGa₅ is Curie-Weiss-like, with an effective moment expected for a nearly localized 5f⁵ configuration. Because the presence of a local moment is detrimental to conventional superconductivity, this suggests the possibility that superconductivity of PuCoGa₅ is unconventional, e.g. mediated by a magnetic interaction, which is the case in strongly correlated electron materials, such as the high- T_c cuprates and heavy-fermion systems based on Ce or U. This possibility is borne out by NMR measurements^{2,3} that find a power-law dependence of the nuclear-spin relaxation rate $1/T_1$ in the superconducting state of PuCoGa₅ as well as in the isostructural superconductor⁴ PuRhGa₅ with $T_c=8.5$ K. Further, $1/T_1$ in the normal states of these materials also is unconventional and consistent with nuclear-spin relaxation being dominated above T_c by the presence of 5f-electron spin fluctuations. Together, these experiments lead to a picture of superconductivity mediated by magnetic fluctuations associated with Pu's 5f electrons whose characteristic spin fluctuation rate is set by hybridization with ligand electrons. This interpretation also is consistent with the suppression of T_c with self-radiation damage, the temperature dependence of electrical resistivity, the large value of a magnetic field required to suppress superconductivity, and an enhanced Sommerfeld coefficient of specific heat that are found in these Pu superconductors.

Hybridization of 5f and ligand electrons not only sets the characteristic energy scale for spin fluctuations but also the bandwidth of electronic states at the Fermi energy E_F . In a simple approximation, the inverse of the bandwidth is proportional to the density of electronic states at E_F measured by the Sommerfeld specific heat coefficient. The superconducting transition temperatures of Ce- and U-based heavy-fermion compounds, the high- T_c cuprates and these Pu superconductors appear to have a common linear dependence on the energy scale set by hybridization.² The T_c 's of PuCoGa₅ and PuRhGa₅ are intermediate to those of these two other families of superconductors, implying that the 5f electrons of the Pu superconductors are not as localized as the f-electrons in heavy-fermion systems but more localized than the d-electrons of the cuprates. This is the same correlation expected on the basis of the spatial extent of the relevant f- or d-electrons and equivalently of their effective bandwidth or Sommerfeld coefficient. Extending this picture to elemental Pu suggests that its 5f electrons are strongly hybridized with band electrons, preventing it from being either superconducting or magnetic.

Besides superconductivity, are there other surprises waiting to be found in PuCoGa₅ or PuRhGa₅? The answer is almost certainly yes. One possibility comes from a comparison with the isostructural heavy-fermion compounds CeCoIn₅ and CeRhIn₅ in which hybridization can be tuned by readily accessible pressures and magnetic fields. Though CeCoIn₅ is superconducting at atmospheric pressure, CeRhIn₅ is antiferromagnetic but becomes superconducting with applied pressure. Imposing a magnetic field on CeRhIn₅ in its superconducting state induces magnetic order that is hidden by superconductivity in the absence of a field.⁵ Various theoretical models have been proposed for how this can happen, but the observation of field-induced magnetic order coexisting with superconductivity remains unresolved. The unusual temperature dependence of the nuclear-spin relaxation rate in PuRhGa₅ is strikingly similar to that of CeRhIn₅ under pressure, suggesting that the relative f-electron hybridization is comparable in both materials which also is true for PuCoGa₅ and CeCoIn₅. From this comparison, it seems worthwhile to search for field-induced magnetism in PuRhGa₅, which, if found, would allow a new approach to probing the nature of plutonium's 5f-electrons and its evolution with field tuning.

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Futuristic back-end of the nuclear fuel cycle with the partitioning of minor actinides

by

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The reprocessing of nuclear spent fuels is industrially carried out in several countries in the world. The most important reprocessing facility is situated in France at La Hague (Aréva-Cogéma Company). Today, the aims of the reprocessing are: i) to recover the elements U and Pu which have large potentiality to produce more energy and which can be recycled as new fuels (MOX fuel for the recycled Pu), ii) to condition the nuclear wastes into solid matrices. Most of the radionuclides from the wastes are conditioned in glass. The glasses contain most of the Fission Products (FPs) and the minor actinides (MAs): Np, Am and Cm. These glass wastes will be in the future disposed of into deep geological repositories. But, the most difficult problem to define such deep geological repositories is related to the very important radiotoxicity of these glass wastes which stay very important for about 100,000 years. This is mainly due to the presence of the MAs in these glass wastes. So, a new strategy is under consideration in numerous nuclear countries: if the MAs are eliminated from the glass wastes, the definition of a deep geological repository will be more simpler. After their partitioning, the MAs can be considered as destructible by nuclear facility, such as the ADS. So, in France and in Europe, important research for MAs partitioning are done. Most of the work done was in the domain of hydrometallurgy. The most important results obtained in Europe will be presented here.

Separation of neptunium (Np)

In the spent fuel aqueous nitric acid dissolution liquor, Np exist on Np(V) (NpO_2^+) and Np(VI) (NpO_2^{2+}) forms. In order to co-extract Np with U(VI) and Pu(IV) by the TBP within the PUREX process, it is necessary to convert all the Np into its Np(VI) form which possesses a high affinity for the TBP. In order to do so, at the CEA-Marcoule, it was shown that if the $[\text{HNO}_3]$ of the dissolution liquor is higher than that used in the industrial plant at La Hague (3 M HNO_3), Np can be totally converted to Np(VI) in presence of the TBP solvent, and then Np can be co-extracted with U(VI) and Pu(IV). Such a demonstration was successfully demonstrated at CEA-Marcoule in 2005, during the treatment by the PUREX process of 14 kg of spent UOX fuel.

Separation of americium (Am) and curium (Cm)

As Am and Cm exist in the spent fuel aqueous dissolution liquor as trivalent actinide ions (An): Am(III) and Cm(III), it was necessary to design new extractant able to co-extract An(III) from the nitric acid raffinate issuing the PUREX process. Moreover, as about a third

of the FPs is composed of trivalent lanthanides ions (Ln(III)), the co-extraction of An(III) + Ln(III) is obtained. So, after the co-extraction of An(III) + Ln(III) a separation An(III)/Ln(III) should be done.

DIAMEX process. For the co-extraction of An(III)+ Ln(III) nitrates from High Active Wastes, a lot of work has been done to select a new extracting agent. The family of malonamide molecules was chosen and among more than 100 ligands tested, the DMDOHEMA was selected for the so-called DIAMEX process. The DIAMEX process was successfully tested on High Active Raffinate (HAR) both at CEA-Marcoule and at the ITU (Karlsruhe, Germany). Moreover, at the ITU, the DIAMEX process was also successfully tested using High Active Concentrate (concentration factor vs HAR of 10).

SANEX process(es). For the separation of An(III) vs Ln(III) issuing the DIAMEX process, it was necessary to define very specific extractants able to selectively extract the An(III). In this very difficult domain, several processes were designed including: i) SANEX process based on the tridentate N-ligand *iPr*-BTP, and ii) synergistic mixture of *bis*-chlorophenyl-*di*-thiophosphinic acid ((ClPh)₂PSSH) + TOPO. Hot tests of the SANEX process using BTP ligands was done at CEA-Marcoule and at the ITU. If good results were obtained, unfortunately, it was demonstrated that the BTP extractants are not sufficiently resistant vs radiolysis to be chosen as industrial extractant. The SANEX process based on (ClPh)₂PSSH + TOPO mixture was successfully tested on synthetic spiked solutions at FZ-Jülich (Germany). It should be mentioned that recently a new SANEX system has been defined by CEA and successfully tested in 2005 with real HAR.

Cm/Am separation.

As it will be difficult to destroy Cm nuclides, it was considered necessary to define an Am(III)/Cm(III) separation process. As the malonamide DMDOHEMA possesses a slight higher affinity for Am(III) vs Cm(III) ($SF_{Am/Cm} = 1.6$), a DIAMEX-2 process was defined and successfully tested at CEA-Marcoule with real hot feed.

Most of the work described herein was done within the PARTNEW European Integrated Project (IP) of FP-5. Now, since 2004, the research continues in Europe within the IP EUROPART (FP-6), which incorporates not only MAs partitioning work in hydrometallurgy, but also in pyrometallurgy.

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Thermostatics and Kinetics of Transformations in Pu-based Alloys

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INTRODUCTION

Despite the recent progress made in predicting the impact of electron localization on the stability of the δ (or fcc) phase of Pu, an accurate determination of the energetics for pure Pu and its alloys still offers paramount challenges. As a viable alternative, the CALPHAD (CALCulation of Phase Diagrams) methodology¹ has been extremely successful since the 70's in describing the thermodynamics of complex multi-component alloys. Hence, before input from *ab initio* calculations to the thermodynamic database becomes a reality, statics and kinetics of phase transformations in a series of Pu-based alloys have been investigated² with CALPHAD with reference to experimental data only. Here we summarize some of the most salient conclusions of this study for the Pu-Ga alloy system.

STATICS OF PHASE TRANSFORMATIONS

In the 80's attempts have been made to assess the phase stability properties of Pu-Ga alloys by focussing on the Pu-rich part of the phase diagram³. However, since stability is a global property that requires an accurate knowledge of alloy behaviour in the whole range of composition, a new assessment was performed. The input data consisted of the phase diagram and the heats of formation of the compounds measured experimentally. Since the emphasis was put mostly on the high-temperature phase diagram data, the low temperature alloy behaviour comes out as a prediction from this assessment. As shown in Fig. 1, besides the overall agreement with the known experimental phase diagram, an eutectoid-phase decomposition is predicted at about 57 °C in the Pu-rich portion of the phase diagram in agreement with the Russian experimental results⁴. It is worth noting that the CALPHAD boundary of the two-phase region (δ +Pu₃Ga) lies on the left (*i.e.*, at lower Ga composition) of the experimental results. This finding was expected since the slow kinetics of formation of Pu₃Ga precipitates in the fcc matrix at low temperatures precludes the observation of small phase fraction of Pu₃Ga.

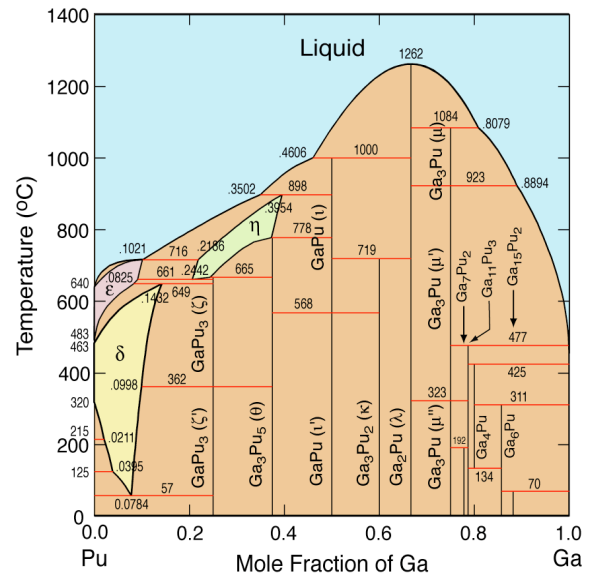


Figure 1. CALPHAD assessment of the Pu-Ga phase diagram.

KINETICS OF PHASE TRANSFORMATIONS

Kinetic modeling was applied to the study of diffusion-controlled transformation in the case of the eutectoid reaction $\delta \rightarrow \alpha + \text{Pu}_3\text{Ga}$ with the thermodynamic driving force obtained from the previous results and a mobility database built upon available experimental data. The temperature-time-transformation (TTT) curves are shown for the two separate reactions in Fig. 2. Close to the temperature of eutectoid decomposition, the time for transformation is about $1.5 \cdot 10^6$ years. Hence, although the “American” version of the phase diagram describes metastable equilibrium, the actual equilibrium eutectoid transformation is definitely inhibited by diffusion alone.

To study the early stage of the $\delta \rightarrow \alpha$ isothermal martensitic transformation, the model of martensite nucleation proposed by Cohen and Kaufman (CK)⁵, and successfully applied to Fe-Ni alloys, was adopted. In this model, the main idea is that a heterogeneity must pre-exists beyond a critical size, and to rapidly transforms in a martensite this embryo must go through a number of growth steps that are thermally activated. In the present case, a rate control reaction at the highest Ga contents was proposed to explain the transition from single to double C-shape of the TTT curves with an increase in Ga content. The results shown in Fig. 3 account for the change in time scale of the early stage of martensite nucleation with alloy composition, in agreement with those from Orme *et al.*⁶

This work was performed under the auspices of the U. S. Department of Energy by the University of California Lawrence Livermore National Laboratory under Contract W-7405-ENG-48.

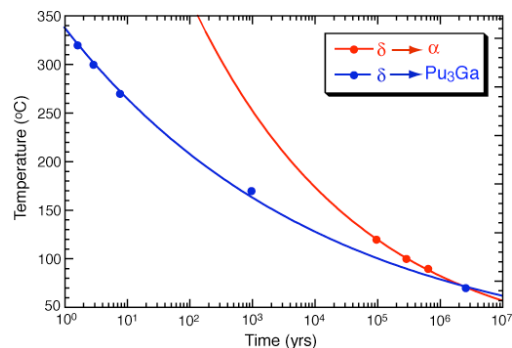


Figure 2. Calculated TTT curves for a δ matrix of $\text{Pu}_{1-x}\text{Ga}_x$ alloys transforming into the α phase, with a transformation rate of 5%.

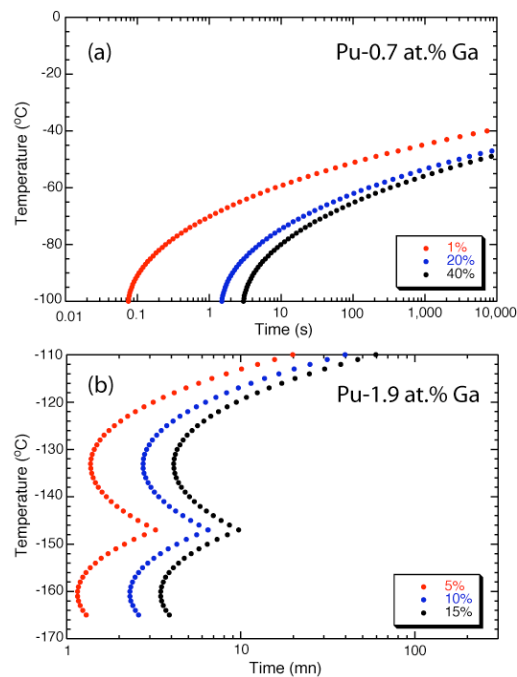


Figure 3. TTT curves associated with various rates of transformation for Pu-Ga alloys with (a) 0.7 and (b) 1.9 at.% Ga.

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Zirconia inert matrix for plutonium utilisation and minor actinides disposition in reactors.

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The toxicity of the UOX spent fuel is dominated by plutonium and minor actinides (MA): Np, Am and Cm, after decay of the short live fission products. Zirconia ceramics containing Pu and MA in the form of an Inert Matrix Fuel (IMF) could be used to burn these actinides in Light Water Reactors and in High Temperature Reactors. Optimisation of the fuel designs dictated by properties such as thermal, mechanical, chemical and physical must be performed with attention for their behaviour under irradiation. Zirconia must be stabilised by yttria to form a solid solution such as $An_zY_yPu_xZr_{1-y}O_{2-y}$ where minor actinide oxides are also soluble. Burnable poison such as Gd, Ho, Er, Eu or Np, Am them-self may be added if necessary. These cubic solid solutions are stable under heavy ion irradiation. The retention of fission products in zirconia, under similar thermodynamic conditions, is a priori stronger, compared to UO_2 , the lattice parameter being larger for UO_2 than for $(Y,Zr)O_{2-x}$. $(Er,Y,Pu,Zr)O_{2-x}$ in which Pu contains 5% Am was successfully irradiated in the Proteus reactor at PSI, in the HFR facility, Petten as well as in the Halden Reactor. These irradiations make the Swiss scientists confident to irradiate such IMF in a commercial reactor that would allow later a commercial deployment of such a fuel for Pu and MA utilisation in a last cycle. The fuel forms namely pellet-fuel, cermet, cermet and coated particle fuel are discussed considering the once through strategy. For this strategy, low solubility of the inert matrix is required for geological disposal. As spent fuels these IMFs are demanding materials from the solubility point of view, this parameter was studied in detail for a range of solutions corresponding to groundwater under near field conditions. Under these conditions the IMF solubility is 10^6 times smaller than glass, which makes the zirconia material very attractive for deep geological disposal. The desired objective would be to use IMF to produce energy in reactors, opting for an economical and ecological solution. The Swiss IMF results are reported in the proceedings of the IMF workshops published in J. Nucl. Mater. (1999, 2003 & 2006) and Prog. Nucl. Energy (2001).

The theory of electronic structure and magnetic properties of Pu and Pu alloys

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The key question in understanding plutonium properties is a problem of $5f$ -electrons localization. For the actinides on the right side of Pu in periodic table starting from americium $5f$ -electrons are fully localized while for the left side elements they are itinerant and contribute to the chemical bonding resulting in a much smaller atomic volume. Pu itself can be as in small volume state (α phase) as well as in large volume state (δ phase). Density functional theory calculations describe well small volume phase but in order to reproduce large volume phase a strong spin-polarization of $5f$ -electrons is needed. That is in contradiction with experimental data showing that there are no local magnetic moments of Pu ions. There are two ways to explain the absence of magnetic moments on localized $5f$ electrons. One is Kondo type screening due to the hybridization of $5f$ electrons with s -, p - and d -electrons. This effect can be described in Dynamical mean-field theory calculations. Another explanation come from the taking into account very strong spin-orbit coupling in this material that can lead to the f^6 configuration with a zero value of total magnetic moment. In the talk a review will be given of various attempts to describe electronic structure and magnetic properties of Pu and Pu alloys in *ab-initio* calculations.

Solubility and Redox Equilibria of Plutonium

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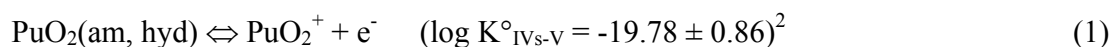
The redox behavior of Pu, the hydrolysis of Pu(IV), and the solubility of Pu(IV) hydrous oxide in the presence of oxygen are discussed controversially in the literature. Experimental results are often ascribed to radiolysis or kinetic effects, disproportionation reactions, etc. We have studied the redox behavior of Pu(IV) solutions at pH 0 – 2 as function of time and the solubility of Pu(IV) hydrous oxide at pH 2 – 13 (under Ar + traces O₂) using Pu-242. The redox potential, in many literature studies not measured or considered as not reliable, is found to be a key parameter for the understanding of the aqueous Pu chemistry. With the known equilibrium constants for the system Pu/e⁻/H⁺/OH⁻/NaCl or NaClO₄/H₂O (25°C)^{1,2} and additional data determined for PuO_{2+x}(s,hyd) and small Pu(IV) colloids/polymers (1.5 – 2 nm), which are part of the thermodynamic system, the total Pu solubility and oxidation state distribution is explained consistently in terms of equilibrium thermodynamics.

REDOX BEHAVIOR AND HYDROLYSIS OF Pu(IV) IN ACIDIC SOLUTIONS

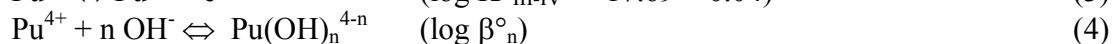
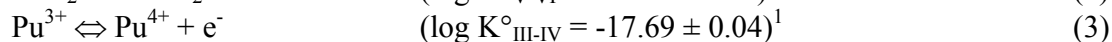
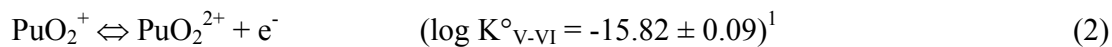
Electrochemically prepared Pu(IV) stock solutions were diluted to 10⁻⁵ to 5·10⁻⁴ M Pu(IV) solutions at pH_c = 0.3 - 2.1 in 0.5 M HCl/NaCl. The concentrations of Pu(IV)_{aq}, Pu³⁺, PuO₂⁺ and PuO₂²⁺ were determined by UV/Vis/NIR absorption spectroscopy, using a 1m-capillary cell for low concentrations. The presence or absence of Pu(IV) colloids > 5 nm was confirmed by LIBD³. The oxidation state balance determined by spectroscopy and LSC in solutions free of colloidal Pu(IV) demonstrates that the Pu(IV) absorption band at 470 nm remains unaffected by mononuclear hydrolysis reactions in the pH range 0 – 2. The decrease in the molar absorbance is only caused by the formation of polymeric/colloidal species Pu(IV)_{coll}.

The redox behavior of acidic Pu(IV) solutions is usually ascribed to the disproportionation of 2 Pu(IV) into Pu(III) and Pu(V) and/or of 3 Pu(IV) into 2 Pu(III) and Pu(VI). Accordingly, at any time the following balance must be valid: [Pu(III)] = [Pu(V)] + 2 [Pu(VI)].⁵ However, doubts on this reaction path^{3,4} are confirmed: None of the investigated solutions fulfills this balance at reaction times < 10 days. Instead, the formation of Pu(III) is equal to the simultaneous decrease of Pu(IV)_{aq}, (d[Pu(III)]/dt = - d[Pu(IV)_{aq}]/dt), i.e., {[Pu(IV)_{aq}] + [Pu(III)]} = constant and, as a consequence: d{[Pu(V)] + [Pu(VI)]}/dt = - d[Pu(IV)_{coll}]/dt.

These results indicate that the so-called ‘disproportionation of Pu(IV)’ is a two-step process. The initial step is the formation of PuO₂⁺, either by the oxidation of colloidal or polynuclear Pu(IV) species by O₂ or due to the redox equilibrium with Pu(IV) colloids > 5 nm which have thermodynamic properties equal to PuO₂(am, hyd)⁶:



The second step is the simultaneous equilibration of the redox couples Pu(V)/Pu(VI) and Pu(IV)/Pu(III) which are related by pe (and pH because of Pu(IV) hydrolysis equilibria):



The oxidation state distributions and redox potentials ($\text{pe} = 16.9 \text{ Eh(V)}$ at 25°C) measured after more than 20 days are consistent with known ‘disproportionation’ equilibria⁴⁻⁶ which correctly describe the equilibrium state, but not the underlying reaction mechanism.

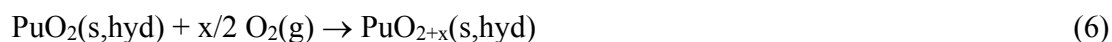
Combining reactions (3) and (4) allows to determine $\log \beta_n^{\circ}(\text{Pu(OH)}_n^{4-n})$ from the relation:

$$\text{pe} + \log ([\text{Pu}^{3+}]/[\text{Pu(IV)}_{\text{aq}}]) = -\log K_{\text{III-IV}} - \log (1 + \sum \beta_n^{\circ} [\text{OH}^-]^n) \quad (5)$$

The spectroscopically determined concentrations of Pu^{3+} and $\text{Pu(IV)}_{\text{aq}}$ and the measured redox potentials (consistent with pe values calculated from $\log K^{\circ}_{\text{V-VI}}$ and the spectroscopically determined Pu(V) and Pu(VI) concentrations) yield the following hydrolysis constants, corrected to $I = 0$ with the SIT: $\log \beta_1^{\circ} = 14.0 \pm 0.2$, $\log \beta_2^{\circ} = 26.8 \pm 0.6$, $\log \beta_3^{\circ} = 38.9 \pm 0.9$). These values are lower than those selected in the recent NEA-TDB review².

SOLUBILITY OF Pu(IV) HYDROUS OXIDE IN THE PRESENCE OF OXYGEN

The total Pu concentrations, oxidation state distributions and redox potentials measured in solubility studies with Pu(IV) hydrous oxide under air (Rai et al.⁷) and under Ar containing only traces of O_2 (present work) indicate that O_2 is scavenged by solid $\text{PuO}_2(\text{s,hyd})$ yielding mixed valent $\text{PuO}_{2+x}(\text{s,hyd}) = (\text{Pu}^{\text{V}})_{2x}(\text{Pu}^{\text{IV}})_{1-2x}\text{O}_{2+x}(\text{s,hyd})$ as proposed by Haschke et al.⁸:



The oxidized fractions of $\text{PuO}_{2+x}(\text{s,hyd})$ (ca. 10 % in the studies of Rai et al.⁷ under air and 0.5 % in the present experiment) are correlated to the amount of oxygen in the system and/or the amount of oxidized Pu in the original Pu(IV) stock solution. At low pH they are completely soluble but at $\text{pH} > 3$, the aqueous Pu(V) concentration is limited to the solubility of $\text{PuO}_{2+x}(\text{s,hyd})$ which may be considered as solid solution $(\text{PuO}_{2.5})_{2x}(\text{PuO}_2)_{1-2x}(\text{s,hyd})$:

$$\log K_{\text{sp}}(\text{PuO}_{2.5} \text{ in } \text{PuO}_{2+x}(\text{s,hyd})) = \log ([\text{PuO}_2^+][\text{OH}^-]) = -14.0 \pm 0.8. \quad (7)$$

The low redox potentials at $\text{pH} 4 - 13$ are reproducible and independent of the initial O_2 in the system. They can be explained by equilibria between $\text{PuO}_{2+x}(\text{s,hyd})$, $\text{PuO}_2^+(\text{aq})$ and small Pu(IV) colloids/polymers (1.5 - 2 nm) which are part of the thermodynamic system and predominant at $\text{pH} > 7$. The molar standard Gibbs energy $\Delta_f G^{\circ}_m(\text{PuO}_{2+x}(\text{s,hyd}))$ derived from the solubility data is considerably less negative than calculated by Haschke et al.⁸ who assumed the oxidation of $\text{PuO}_2(\text{s})$ by reaction with water.

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Nuclear forensics investigations with a focus on plutonium

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ABSTRACT

Since the beginning of the 1990's when the first seizures of nuclear material were reported, IAEA has recorded over 200 cases of illicit trafficking of nuclear materials. The number of nuclear material seizures has decreased drastically from the "record" year of 1994 when 45 seizures were recorded to about 10 seizures per year at the present. However, the issue continues to attract public attention and is a reason for concern due to the hazard associated with such a materials. The radiological hazard arises from inappropriate handling, transport or storage, and even more serious concerns arise if considered in a terrorist context. Nuclear material can either be used in a radiological dispersal device, so-called "dirty bomb" or - if available in sufficient quantity and quality - in nuclear explosive devices.

Once illicitly trafficked nuclear material has been intercepted, the following questions are to be addressed: What was its intended use? Where is its origin and who was its last legal owner? Especially the origin is of prime importance in order to close the gaps and improve the physical protection at the sites where the theft or diversion occurred. The analytical strategy is following a step-by-step approach, where based on actual findings the next step is defined and performed.

Analytical methods adapted from nuclear safeguards serve as a basis in nuclear forensic analysis. However, it was soon noticed that they were not sufficient to provide answers to all the questions. Therefore, dedicated nuclear forensic methodology has been developed. This approach combines methods used in nuclear fuel cycle, materials research and environmental studies, including radiometric and mass spectrometric techniques as well as electron microscopy. The conclusions from such investigations need to be supported by reference data whenever possible.

The Institute for Transuranium Elements (ITU) has been involved nuclear forensics research since the beginning. During the last ten years, methods for the age determination of U and Pu, the geolocation of natural U, and the determination of the reactor type from the Pu isotopic composition have been developed. In addition to that some 30 samples originating from real seizures of nuclear material have been analyzed. In this paper, an overview is given on the methodologies used, on the past and on-going developments and on the experience gathered. Some selected examples shall illustrate the challenges and the complexity associated with this work.

How the *f* electrons hide

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When the *f* electrons seem to come and go in cerium, at least a magnetic moment comes and goes; so things look simple. In plutonium the magnetism that should be there, never shows up. These questions will be reviewed. Recent results will be shown that tie together neutron scattering, photoemission, and thermodynamic measurements. Along with other work, we can put some limits on models of *f*-electron behavior. It does seem as if we have made some progress after years of drought.

Insights into the bonding and electronic nature of heavy element materials

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ABSTRACT

A long standing issue in heavy element science is what role electrons, especially the f electrons, play in chemical and physical behaviors. This interest prevails not only for differences between the two different f-electron series and but also for comparing a particular element's behavior in its elemental and combined states.

Different types of experimental results over the years have been employed to probe and evaluate the nature of bonding and electronic configurations in these materials. In some instances the conclusions arrived at from experiment and theory has differed, but recently both theory and experimental techniques have become more encompassing and sophisticated.

Interpretations about the electronic interactions and bonding at ambient or elevated temperatures in the f-elements have been employed for many years and have generated information under these conditions. More recently, structural behaviors under pressure and the associated correlations with bonding via experimental methods have become especially enlightening, and have resulted in surprising results. These experimental findings also generated increased theoretical efforts to probe and understand these changes, as well as offer new insights. Modern experimental and theoretical approaches in this arena alone have improved dramatically and now offer improved accuracies and detailed insights.

The changes in bonding and the electronic behavior of metals and alloys from the application of pressure provide different insights into the materials than examined by other techniques and under different conditions. The decreasing interatomic distances occurring under pressure alter energy levels and may provide a different potential for the overlap or hybridization of electronic orbitals. In contrast, changes observed in compounds under pressure may or may not reflect the involvement or a participating role for the f electrons. This difference with compounds probably reflects the presence and different bonding roles of the non-f element atoms, which affect not only the interatomic f-element distances but also the type of electronic orbitals encountered that can potentially interact.

Experimental results obtained from applying pressure are known for Th, Pa, U, Np, Pu, Am, Cm, Bk, and Cf, and attempts have been made to study Es. Several aspects of these elements' behaviors under pressure have also been considered theoretically, and in several instances theory and experiment have now become in accord. The recent findings with curium under pressure are exceptionally interesting, as it displays a unique

phase stabilized due to the magnetic influence of its 5f electrons¹. Yet, there remain some interesting differences between experimental and theoretical interpretations of the changes observed with americium²⁻⁷, which arises from aspects of the “fine tuning” used in the interpretations.

Different aspects of results obtained to date for f-electron materials using different experimental approaches and conditions will be examined and discussed here with regard to electronic configurations and potential changes in bonding. In addition, prospects for future efforts, the potential findings envisioned for these f-electron metals and compounds, and the effects on their fundamental and technological science offer intriguing science for the future. The different prospects presented here will also serve as introductory comments for presentations in the following sessions.

ACKNOWLEDGEMENT

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Density changes of δ - plutonium with alloying elements and with aging.

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Experiments are conducted at several laboratories to monitor the dimensional changes of Pu-Ga alloys with time, with temperature, and with the alloy composition. Measurements are performed by x-ray diffraction, by EXAFS, by dilatometry, and by immersion density. The dimensional changes attributed to the radioactive decay of plutonium are divided into four processes:

- 1) An initial transient expansion that manifest itself as an increase in both the lattice parameter and the length of a specimen. This expansion is reversible as it can be annealed by heating the material to a temperature above about 450 K.
- 2) A gradual long-term expansion that is attributed to the in-growth of helium bubbles and to the accumulation of actinide daughter products.
- 3) Radiation-induced void swelling is a possible process but has so far not been observed.
- 4) Transformation of the metastable Pu-Ga δ -phase.

We review the experimental data and evidence for each of these four processes and discuss recent theoretical and computational work to explain the data or to predict what might be observed in future experiments.

The transient expansion of plutonium-gallium alloys observed both in the lattice parameter as well as in the dimension of a sample held at ambient temperature is explained by assuming incipient precipitation of Pu₃Ga. However, this ordered ζ' -phase is also subject to radiation-induced disordering. As a result, the gallium-stabilized δ -phase, being metastable at ambient temperature, is both driven towards thermodynamic equilibrium by radiation-enhanced diffusion of gallium and at the same time pushed back to its metastable state by radiation-induced disordering. A steady state is reached in which only a modest fraction of the gallium present is tied up in the ζ' -phase.

Next, we discuss the analysis of irreversible volume changes due to the accumulation of helium and daughter products generated in the radioactive decay of plutonium. It is shown that the lattice parameter changes in δ -phase plutonium caused by Am, U, and Np are significant and compensate to some degree the swelling from helium bubble formation and growth. Comparison with experimental results obtained so far suggests that the decay products dominate the rate of volumetric change in the long run.

The absence of voids or any other observable radiation-induced defects (other than helium bubbles) is discussed in terms of dose rate effects, vacancy migration, nature of the self-interstitial, and dislocation bias. Several of these factors indicate that void swelling is unlikely to occur in Ga-stabilized δ -plutonium.

Plutonium Science Futures

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Much was anticipated at the discovery of plutonium in 1941 in Berkeley, but initially the chemical and metallurgical properties were completely mystifying. By the mid 1960s the physical properties, even at low temperature were reasonably well characterized. With a few notable exceptions, e.g. photoemission, *most* properties of Pu were known by the 1970 Conference in Sante Fe. However, these properties of Pu continue to test our basic understanding even today. Actinide science has flourished in the last 50 years, and very often Pu is at the heart of it – take, for example, the recent discovery of superconductivity at 18 K in a Pu-containing compound.

This overall activity, crucial for the underpinning of nuclear technology, is at risk due to the ever-tightening regulations and difficulty of access. Of course, we cannot have Pu in every University Laboratory, but we must find a way to keep research on plutonium chemistry and physics alive and diversified, and more people interested in the basic properties, chemical and physical, of the transuranium materials. The political consequences of the actinides will not “go away” by pretending Pu does not exist.

For presentation at the “Plutonium Futures – The Science 2006”
Asilomar, CA, July 12, 2006

“Plutonium World Futures”

Siegfried S. Hecker

Center for International Security and Cooperation

Stanford University

For presentation at “Plutonium Futures – The Science 2006

Asilomar, CA

July 12, 2006

In addition to being the most complex element in the periodic table, plutonium also has great societal impact. It has become to symbolize everything we associate with the nuclear age. It evokes the entire gamut of emotions from good to evil, from hope to despair, and from the salvation of humanity to its utter destruction. No other element bears such a burden. Its discovery in 1941, following the discovery of nuclear fission in 1938, unlocked the potential and fear of the nuclear age. During the Cold War, plutonium was of interest primarily for nuclear weapons and deterrence. Beginning in the 1950s, it also became an integral part of the quest for almost limitless electrical power. Today, concerns over energy availability and global climate change have rekindled interest in nuclear power. However, to benefit from the factor of millions that splitting the atom provides, we must tackle the challenges posed by concerns about the proliferation of nuclear weapons, the disposal of nuclear waste, and the cleanup of nuclear contamination at the world's weapons sites. We can't just make plutonium go away – so we must learn to manage it, and this has to be a cooperative international venture.